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Investigating the Adsorption of Berry and Mango Leaf Extract Inhibitors on the Copper Surface in NHO_3 Solution

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Keywords:

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ABSTRACT

Corrosion inhibition of copper material of oil pipelines in (1 M) nitric acid solution was used as part of a prior study using *Berry & Mango Leaves Extract* inhibitors. The effect of both the temperature and the concentration of these inhibitors have been considered. The inhibitory impact was taken into consideration by varying the inhibitor concentrations (50, 100, 150, 200, 250, and 300 ppm by weight of the solutions). The measurements' findings demonstrated that (BMLEs) had a respectable level of corrosion inhibition, with maximal inhibitor efficiencies of roughly 74 % and 83 % for berry and mango leaves, respectively. In the present paper work a further calculation has been done in order to investigate the adsorption of *Berry & Mango Leaves Extract* inhibitors on the surface of copper material. The adsorption experiment made use of a number of adsorption isotherms, including Langmuir, Temkin, Freundlich, Adejo Ekwenchi, El—Awady, Flory-Huggins, Fowler-Guggenheim and Kiselev. The *Berry & Mango Leaves Extract* inhibitors have been found obeying with most of the used isotherm models, which indicating that the inhibitors have an excellent adsorption on the copper surface. On the other hand, (ΔG°_{ads}), revealed that the adsorption mechanism of inhibitors on the copper surface was spontaneous and physisorption.

الكلمات المفتاحية:

معدن النحاس
مستحلب أوراق التوت
مستحلب أوراق المانجو
أنابيب النفط
نماذج مقاييس الإمتزاز
التغطية السطحية للمثبط

دراسة امتزاز مثبطات مستخلص أوراق التوت والمانجو على أسطح النحاس في محلول حمض النيتريك باستخدام معاملات الديناميكية الحرارية ونماذج الإمتزاز الأيزوثرمية.

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الملـخص:

في دراسة سابقة تم استخدام مثبطات مستخلص أوراق التوت والمانجو لدراسة تآكل كلاً من معدن النحاس لخطوط أنابيب النفط في محلول حمض النيتريك. بالإضافة الى ذلك تم الأخذ في عين الإعتبار تأثير كلاً من درجة الحرارة وتراكيز هذه المثبطات. تم أستخدام تراكيز مختلفة (50 ، 100 ، 150 ، 200 ، 250 ، و 300 جزء في المليون). من خلال نتائج الإختبارات تبين أن هذه المثبطات لها درجة مقبولة للحماية من التآكل, حيث وجد أن أقصى كفاءة لمثبط ورق التوت على سطح معدن النحاس حوالي 74%, بينما أقصى كفاءة لمثبط ورق المانجوعلى سطح النحاس حوالي 83%. في البحث الحالي, تم دراسة درجة أمتزاز هذه المثبطات على سطح النحاس وذلك بأستخدام معاملات الديناميكا الحرارية وكذلك بعض نماذج الإمتزاز الإيزوثرمية, وتشمل كلاً من: لانجمويز وتيمكين وفروندليش وأديجو إكوينشي والعوادي وفلوري هوجينز ، وفولر-غوغنهايم ، وكيسيليف. بينت قيم معامل الأرتباط لنماذج الأمتزاز الأيزوثرمية أن كلاً من مستحلب أوراق التوت والمانجا ثمار البلوط المثبط تتوافق مع معظم نماذج الأمتزاز الأيزوثرمية، وكان المثبطين أكثر توافقاً فقط مع نموذج تمكين. يخلص البحث الى أن درجة إمتزاز المثبط على سطح الحديد النحاس فعال جداً, وآلية الإمتزاز للمثبطات المستخدمة في هذا البحث كانت آلية فيزيائية.

1. Introduction

Considering the research conducted in (2022) by *Hamdy Matter* and *Tarek Ayad* [1], which evaluated the effect of *Berry & Mango Leaves Extract* inhibitors on the corrosion behaviour of copper oil pipelines in (NHO_3) setting. It was discovered that the weight loss and corrosion rates as well as the inhibitor efficacy changed with the inhibitors concentrations, when copper material was exposed to the inhibitors. The minimal corrosion rate for Berry Leaves Extract inhibitor on the copper surface in (1M NHO_3) at room temperature was measured as (30 $mg.cm^{-2}.hr^{-1}$) at the maximum used inhibitor concentration (300 ppm) and for *Mango Leaves Extract* on the copper surface in (1M) NHO_3 at room temperature was measured as (24 $mg.cm^{-2}.hr^{-1}$) at the maximum used inhibitor

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concentration (300 ppm), while the highest corrosion inhibition efficiency was found to be (75%) and (80%) for *Berry* and *Mango Leaves Extract* inhibitors respectively.

The chemical element copper has the atomic number 29 and the letter Cu, which comes from the Latin word cuprum. It is an extremely high thermal and electrical conductivity metal that is soft, malleable, and ductile. buildings), ductility, malleability, atmospheric corrosion resistance, and long-term. A freshly exposed surface of pure copper has a pinkish-orange colour. [2]. Pure copper has a pinkish-orange colour when freshly exposed. [2]. One of the few metals that can exist naturally in a form that is immediately useable is copper (also known as native metals). This resulted in extremely early human use in a number of areas. For heat exchangers, solar collectors, home heating systems, automotive radiators, and other applications needing quick heat transfer across or along a metal segment, coppers, some brasses, bronzes, and copper nickels are often used metals. Coppers, brasses, bronzes, and copper nickels are also utilized for pipes, valves, and fittings in systems that transmit industrial gases, process water, potable water, or other aqueous fluids due to their exceptional ability to resist corrosion [2]. In the presence of chloride ions, copper and its oxides lose some of their thermodynamic stability (Figure 1a) [3]. For instance, both CuCl and $CuCl_2.3Cu(OH)_2$ are stable at certain pH and EH in 1 mol/kg Cl^-. Furthermore, Cu becomes thermodynamically unstable in water at low pH levels, as shown by the fact that the $Cu/CuCl_2$ - equilibrium line crosses the H_2O/H_2 equilibrium line at pH 2-3 for a dissolved copper activity of 10-6 mol/kg [4]. In the presence of sulphide ions, copper is similarly unstable in water (Figure 1b) [5]. At all pH levels, the H_2O/H_2 equilibrium line is crossed by the stability field for copper sulphide (mainly Cu_2S, with potential non-stoichiometric Cu_2-xS species) [4].

Benzotriazole (BTA) is a well-known organic heterocyclic molecule that is highly effective at preventing copper corrosion in neutral or alkaline solutions [6, 7]. It is widely acknowledged that the adsorption of a single BTA molecule on the copper surface and the development of a polymeric film of a (Cu^+BTA) complex are the two steps that cause it to become inhibited in neutral and alkaline solutions [8]. But in an acidic solution, BTA is primarily found as the protonated species $BTAH^+$. Since copper is thought to be positively charged in acidic solution, this protonated species is less strongly chemisorbed to the copper surface [9].

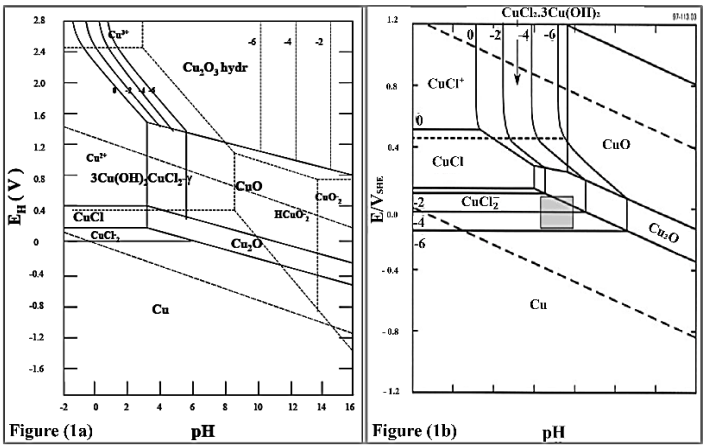

Figure (1a) Pourbaix Diagram for the Copper-Water-Chloride System at 25°C for a Chloride of 1 mol/kg. The Shaded Box Shows the Range of Corrosion Potentials in O_2-Containing Solution [3].

Figure (1b) Pourbaix Diagram for the Copper-Water-Sulphur System at 25°C for a Total Sulphur Concentration of 2·10^-4 mol/kg and a Total Dissolved Copper Concentration of 10^-6 mol/kg [5].

The effectiveness of BTA's inhibition in acidic solutions is consequently reduced as a result of this. Additionally, it has been demonstrated that a few additional heterocyclic compounds are potent inhibitors of copper and its alloys' corrosion. These heterocyclic molecules' toxicity and the fact that the majority of them cannot be biodegraded, however, are very significant drawbacks [10]. Due to this chemical's inability to biodegrade, industrial waste water is released into public waterways, containing significant hazardous material. There is a need for new inhibitors for copper corrosion in acidic media. A possible solution to this problem is to find new ecologically, friendly green corrosion inhibitors. Natural products extracted from plant sources [11], as well as some non-toxic organic compounds, which contain polar functions with nitrogen, oxygen and/or sulphur in conjugated systems in their molecules [12], have been effectively used as inhibitors in many corrosion systems. Amino acids are attractive as corrosion inhibitors because they are relatively easy to

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produce with high purity at low cost and are soluble in aqueous media.

Adsorption isotherm graphs are typically used to study the adsorption process. The amount of adsorbate on the adsorbent as a function of pressure or concentration at a constant temperature is known as adsorption. To enable comparison of various materials, the quantity adsorbed is almost generally normalised by the adsorbent's mass. Because there are just a few vacancies on the surface of the adsorbent, we can infer from the foregoing that adsorption ceases to occur after saturation pressure "Ps". When all of the sites are occupied at high pressure, the adsorption process is no longer affected by pressure increases after that point. Adsorption is pressure independent at high pressures [16]. It is commonly accepted that the first stage in the inhibitors' action mechanism in an aggressive acid media is the adsorption of the inhibitor at the metal solution interface. The adsorption isotherms can have various expressions. It is necessary to fit the analysis of isotherm data into one of the isotherm models in order to construct the adsorption process [16]. In this work, models from Langmuir, Temkin, Freundlich, Adejo Ekwenchi, El-Awady, Flory-Huggins, Fowler-Guggenheim, and Kiselev were used.

2. Results of Corrosion Rate and Inhibitor and Inhibitor Surface coverage Efficiency Related to Reference [1].

According to the results of Ref. [1], Table (1) presents the findings of corrosion tests including corrosion rate, efficiency and surface coverage of *Berry & Mango leaves Extract* inhibitors conducted on copper specimen surface in (1 M) nitric acid solution (HNO_3) at room temperature (25 °C).

Table (1) Corrosion Rate, Efficiency and Surface Coverage of *Berry & Mango Leaves Extract* Inhibitors Related to Ref. [1].

S. No.	Inhibitor (Concentration) I_{inh}, (ppm)	Corrosion Rate (CR) (mg. cm^{-2}. hr^{-1})		Inhibitor Efficiency (IE), (%)		Surface Coverage, (θ)	
		Berry Inhibitor	Mango Inhibitor	Berry Inhibitor	Mango Inhibitor	Berry Inhibitor	Mango Inhibitor
1	Blank	120	120	-	-	-	-
2	050	054	090	55.0	25.0	0.550	0.250
3	100	048	060	60.0	50.0	0.600	0.500
4	150	042	042	65.0	65.0	0.650	0.650
5	200	039	036	67.5	70.0	0.675	0.700
6	250	036	030	70.0	75.0	0.700	0.750
7	300	030	024	75.0	80.0	0.750	0.800

3. Thermodynamic Parameters of Adsorption of *Berry & Mango leaves Extract* in (1 M HNO_3)

The free energy of adsorption, (ΔG°_{ads}), was calculated in order to describe the interaction between adsorbed molecules and metal surfaces.

$$\Delta G^\circ_{ads} = - RT \ln (55.5 \times K_{ads}) \quad (1)$$

where, (55.5) is the concentration of water in solution expressed in (mol. L^{-1}), (K_{ads}) is the adsorption equilibrium constant, (R) is the gas constant (8.314 J. K^{-1}. mol^{-1}), (T) is the absolute temperature in Kelvin, and (R) is the gas constant (8.314 J. K^{-1}. mol^{-1}) [17]. The equilibrium constant (K_{ads}) of adsorption, which may be computed using the fowling equation, and the free energy of adsorption are connected.

$$K_{ads} = (\frac{\theta}{1-\theta}) / I_{inh} \quad (2)$$

Thermodynamic information for the *Berry & Mango leaves Extract* inhibitor in (1 M HNO3) medium, including the adsorption constant (K_{ads}) and adsorption free energy (ΔG°_{ads}), is provided in Table (2) and (Table 3) respectively. The negative value of (ΔG°_{ads}) ensures the stability of the absorbed layer on the electrode surface. The negative values higher than (-40 KJ. mol^{-1}) involve sharing or transferring electrons from the inhibitors to the metal surface to form a co-ordinate type of bond, whereas the positive values up to (-20 KJ. mol^{-1}) are constant with the electrostatic interaction between the charged molecules and charged metal (physisorption) [18]. According to the results in (Table 2&3), the values of adsorbed free energy

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Table (2) (K_{ads}) and (ΔG°_{ads}) of the *Berry Leaves Extract* Inhibitor in (1 M HNO_3).

S. No.	Inhibitor (Concentration) I_{inh},(Mx10^{-4})	$\frac{\theta}{1-\theta}$	Adsorption Constant $(K_{ads}) = (\frac{\theta}{1-\theta})/I_{inh}$ (M^{-1})	Adsorption Energy (ΔG°_{ads}) (KJ. mol^{-1})
1	Blank	-	-	-
2	1.113	1.2222	10981.132	- 33.02
3	2.226	1.5000	6738.544	- 31.81
4	3.339	1.8571	5561.845	- 31.33
5	4.445	2.0769	4672.441	- 30.90
6	5.565	2.3333	4192.812	- 30.63
7	6.679	3.0000	4491.690	- 30.80

Table (3) (K_{ads}) and (ΔG°_{ads}) of the *Mango Leaves Extract* Inhibitor in (1 M HNO_3).

S. No.	Inhibitor (Concentration) I_{inh},(Mx10^{-4})	$\frac{\theta}{1-\theta}$	Adsorption Constant $(K_{ads}) = (\frac{\theta}{1-\theta})/I_{inh}$ (M^{-1})	Adsorption Energy (ΔG°_{ads}) (KJ. mol^{-1})
1	Blank	-	-	-
2	1.184	0.3333	2815.034	- 29.64
3	2.368	1.0000	4222.973	- 30.65
4	3.552	1.8571	5228.322	- 31.18
5	4.736	2.3333	4926.731	- 31.03
6	5.920	3.0000	5067.567	- 31.10
7	7.103	4.0000	5631.423	- 31.36

(ΔG°_{ads}) for *Berry Leaves Extract* Inhibitor in (1 M HNO_3) ranges from (-33.02 KJ. mol^{-1}) to (-30.63 KJ. mol^{-1}), while for *Mango Leaves Extract* Inhibitor in (1 M HNO_3) ranges from (-31.36 KJ. mol^{-1}) to (-29.64 KJ. mol^{-1}). The high and negative sign of the (ΔG°_{ads}) values indicated that there is strong and spontaneous adsorption of both inhibitors on the surface of copper specimens. The both *Berry* and *Mango Leaves Extract* inhibitor systems postulated mechanism are therefore most likely dependent on physical adsorption. In general, hetero atoms in inhibitor molecules, like N/O/S atoms with a single electron, may enhance the adsorption by causing the inhibitor molecules to become electrostatically adsorbed on the metal surface, producing insoluble stable coatings and reducing metal dissolution [19].

4. Adsorption Isotherm Models

4.1. Introduction

The efficiency with which inhibitors bind to surfaces depends on their structural makeup, and it is assumed that this adsorption is directly related to the electrochemical process taking place on the metal surface [20, 21]. The adsorption of the inhibitor molecules from aqueous solution can be thought of as a quasi-substitution process between the organic compound in the aqueous phase, $Org_{(aq)}$, and the water molecules at the electrode surface, $H_2O_{(aq)}$. In this situation, $Org_{(sol)} + xH_2O_{(aq)} = Org_{(aq)}$. The experiment's results can be used to determine how the surface inhibitor interacts with the environment. The sort, amount, charge density, molecular size, interactions between the inhibitor and the metal, and the creation of metallic complexes are all elements that affect the efficiency of the inhibition. Adsorption isotherms give this information. Size, interactions between the metal and the inhibitor, and the creation of metallic complexes are all aspects that affect how effective the inhibition is. Adsorption isotherms give information on how metal inhibitors interact with one another [21]. The adsorption isotherms of Langmuir, Temkin, Freundlich, Adejo Ekwenchi, El—Awady, Flory-Huggins, Fowler-Guggenheim and Kiselev are the most commonly used to determine the mechanism of organo-electrochemical reactions. These are all isotherms of the generic type:

$$f(\theta, x) \exp(-2a\theta) = K_{ads} I_{inh} \quad (3)$$

Where (θ) is the degree of surface coverage, (I_{inh}) is the concentration of the organic inhibitor in the electrolyte, (x) is the size ratio, (a) is the molecular interaction parameter, (K_{ads}) is the equilibrium constant for adsorption, and (f (θ, x) is the configuration factor. The size ratio tells us how many molecules of water are displaced by one molecule of the organic inhibitor. It is frequently believed that the creation and upkeep of a protective coating on the metal surface may prevent corrosion [20]. The formula (IE% = 100 x θ) [21] was used to compute the surface coverage under the assumption that the blocking effects of the adsorbed species account for the majority of the inhibitor efficiency. After the surface coverage data were theoretically fitted into a variety of adsorption isotherms to gain insight into the inhibitor's adsorption process on the surface of copper material, the value of the correlation coefficient (R^2) for each isotherm model was used to select the isotherm that provided the best match [21].

4.2. Langmuir Adsorption Isotherm

The adsorptive capacity of various adsorbents is assessed and compared using the Langmuir isotherm, which

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characterises gas-solid phase adsorption [21]. The relationship between an inhibitor concentration and a material's surface coating is expressed by the Langmuir isotherm as follows: [22]

$$\frac{I_{inh}}{\theta} = \frac{1}{K_{ads}} + I_{inh} \qquad (4)$$

The linear relationship between (log I_{inh}) and (log (I_{inh}) is shown in Figure (2). The parameters of the Langmuir isotherm for *Berry Leaves Extract* and *Mango Leaves Extract* inhibitors are shown in Tables (4) and (5) respectively. The inhibitors for *Berry* and *Mango leaves extract* had (R^2) values of (0.9981) for *Berry Leaves Extract* inhibitor and (0.8245) for *Mango Extract* inhibitor, which show that the *Berry Leaves Extract* is strongly adhered to for *Berry Extract* inhibitor. The *Berry Leaves Extract* inhibitor is more obeying to Lungmir adsorption model comparing to *Mango Leaves Extract* Inhibitor. According to the Langmuir isotherm application to the adsorption of *Berry* and *Mango Extract* inhibitors on the surface of copper in (1 M HNO_3) solution, there is no interaction between the adsorbate and adsorbent, specially for *Berry* and *Mango Extract* inhibitors [23].

Table (4) The Parameters of Isotherm Models for *Berry Leaves Extract* Inhibitor on the Copper Surface in (1 M HNO_3) Solution.

S. No.	log I_{inh}	ln I_{inh}	log θ	log $(\frac{\theta}{1-\theta})$	$\frac{I_{inh}}{\theta}$ x10^{-4}	log $\frac{I_{inh}}{\theta}$
1	-	-	-	-	-	-
2	- 3.9535	- 9.1033	- 0.2596	+ 0.0871	2.205	- 3.6565
3	- 3.6525	- 8.4101	- 0.2219	+ 0.1761	3.767	- 3.4240
4	- 3.4764	- 8.0047	- 0.1871	+ 0.2688	5.215	- 3.2827
5	- 3.3521	- 7.7185	- 0.1707	+ 0.3174	6.891	- 3.1617
6	- 3.2545	- 7.4938	- 0.1549	+ 0.3680	7.950	- 3.0996
7	- 3.1753	- 7.3114	- 0.1249	+ 0.4771	8.905	- 3.0503

Table (5) The Parameters of Isotherm Models for *Mango Leaves Extract* Inhibitor on the Copper Surface in (1 M HNO_3) Solution.

S. No.	log I_{inh}	ln I_{inh}	log θ	log $(\frac{\theta}{1-\theta})$	$\frac{I_{inh}}{\theta}$ x10^{-4}	log $\frac{I_{inh}}{\theta}$
1	-	-	-	-	-	-
2	- 3.9267	- 9.0414	- 0.6021	- 0.4772	4.736	- 3.3246
3	- 3.6256	- 8.3483	- 0.3010	± 0.0000	4.736	- 3.3246
4	- 3.4495	- 7.9428	- 0.1871	+ 0.2688	5.465	- 3.2624
5	- 3.3249	- 7.6551	- 0.1549	+ 0.3679	6.766	- 3.1697
6	- 3.2277	- 7.4320	- 0.1249	+ 0.4771	7.893	- 3.1027
7	- 3.1486	- 7.2498	- 0.0969	+ 0.6021	8.879	- 3.0516

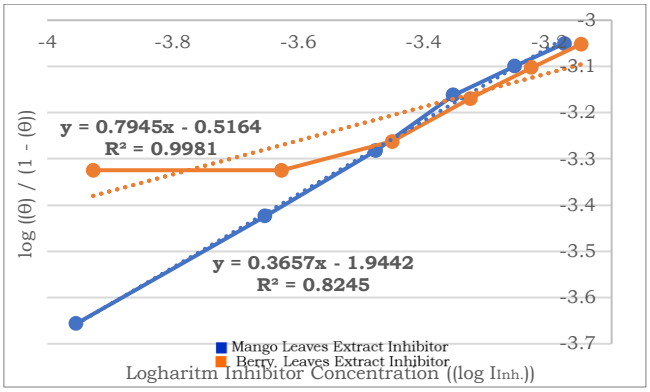
log ((θ) / (1 - (θ)))
y = 0.7945x - 0.5164
R² = 0.9981
y = 0.3657x - 1.9442
R² = 0.8245
Mango Leaves Extract Inhibitor
Berry Leaves Extract Inhibitor
Logharitm Inhibitor Concentration ((log Iinh.))

Figure (2) Langmuir Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

4.3. Temkin Adsorption Isotherm

The Temkin adsorption isotherm's inhibitor concentration (I_{inh}) and coefficient of surface coverage (θ) are correlated by the following equation [24, 25, 26]:

$$\text{Exp.}\ (-2\ a\ \theta) = K_{ads}\ I_{inh} \qquad (5)$$

Tables (1) (4) and (5) display the Temkin isotherm parameters for the inhibitors of *Berry Leaves Extract* inhibitor and *Mango Leaves Extract* inhibitor, respectively.

In Figure (3), plots of (θ) vs. ln (I_{inh}) are shown. The Temkin adsorption isotherm is strongly adhered to for the *Berry* and *Mango Leaves Extract* inhibitors, with the adsorption of *Berry Leaves Extract* inhibitor still being better than that of *Mango Leaves Extract* inhibitor. The inhibitors for *Berry* and *Mango Leaves Extract* inhibitors had (R^2) values of (0.9627) for *Berry Leaves Extract* inhibitor and (0.9850) for *Mango Leaves Extract* inhibitor [29, 30]. It can be seen that both are obeying to Temkin isotherm model, but the latter is more obeying.

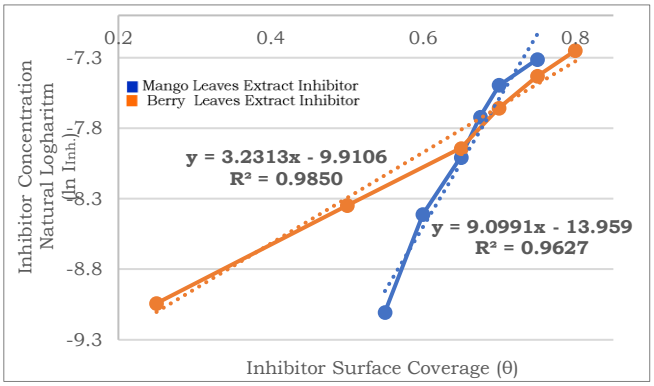
Inhibitor Concentration Natural Logharitm (ln Iinh.)
Mango Leaves Extract Inhibitor
Berry Leaves Extract Inhibitor
y = 3.2313x - 9.9106
R² = 0.9850
y = 9.0991x - 13.959
R² = 0.9627
Inhibitor Surface Coverage (θ)

Figure (3) Temkin Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

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4.4. Frendlich Adsorption Isotherm

The Frendlich adsorption isotherm model has been chosen to calculate the adsorption potential of the absorbent solution. The formula (6) yields the Frendlich isotherm [29].

$$\log\theta + \log K_{ads} + n\log I_{inh} \qquad (6)$$

where n is the parameter for the interaction. Table (3) & (5) displays the Frendlich isotherm's parameters. The plot of log (θ) vs. log (I_{inh}). Plots of log (θ) vs. log (I_{inh}) are displayed in Figure (4). Particularly for the *Berry* and *Leaves Extract* inhibitor, whose adsorption is superior to that of the *Mango Leaves Extract* inhibitor. The (R^2) values for the *Berry* and *Mango Leaves Extract* inhibitors were (0.9777) and (0.9339), respectively. In comparison to the *Mango Leaves Extract* inhibitor, the *Berry Leaves Extract* inhibitor more closely follows the Frendlich isotherm model.

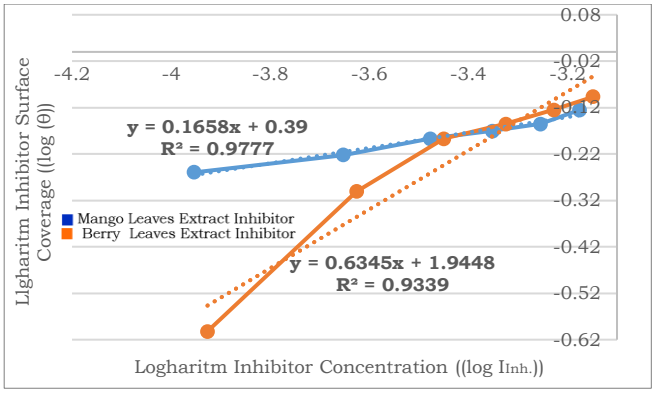

Figure (4) Frendlich Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

4.5. Adejo Ekwenchi Adsorption Isotherm

The difference between the total accessible surface on the adsorbent surface and the proportion that is covered by the adsorbate at that temperature and the amount of adsorbate uptake from the bulk concentration are related in an inverse manner, according to the Adejo Ekwenchi isotherm [30]. Until the surface cover reaches its maximum value, this relationship continues valid. In light of the equation:

$$\log (1/1-\theta) = \log K_{ads} + b \log I_{inh} \qquad (7)$$

Where b parameter is used to determine the mode of adsorption of an inhibitor on the metal surface. The parameters of Adejo Ekwenchi isotherm model are shown in Table (6).

Table (6) The Parameters of Adejo Ekwenchi Isotherm Model for Adsorption of *Berry & Mango Leaves* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

S. No.	*Berry Leaves Extract*		*Mango Leaves Extract*	
	$\frac{1}{1-\theta}$	$\log(\frac{1}{1-\theta})$	$\frac{1}{1-\theta}$	$\log(\frac{1}{1-\theta})$
1	-	-	-	-
2	0.34679	2.22222	0.12493	1.33333
3	0.39794	2.50000	0.30103	2.00000
4	0.45593	2.85714	0.45593	2.85714
5	0.48812	3.07692	0.52288	3.33333
6	0.52288	3.33333	0.60206	4.00000
7	0.60206	4.00000	0.69897	5.00000

Table (4) displays the Adejo Ekwenchi isotherm's parameters. Figure (5) shows a plot of log (1/1- θ) vs. log (I_{inh}) reveals a linear relationship with a (R^2) value of 0.8631 and (0.9198) for the *Berry* and *Mango Leaves Extract* inhibitors, those values demonstrating that the isotherm for the adsorption of *Berry* and *Mango Leaves Extract* inhibitors on the surface of copper are not close to unity, Thus, the both inhibitors are not obeying the Adejo Ekwenchi isotherm model.

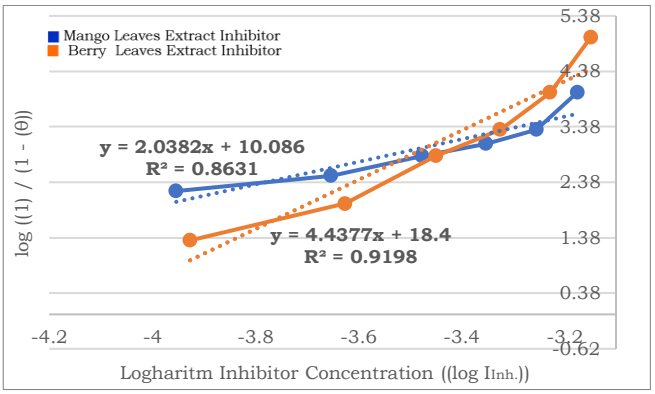

Figure (5) Adejo Ekwenchi Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

4.6. El-Awady Adsorption Isotherm

The El-Awady isotherm model was used to fit the experimental data, and one characteristic of the model is shown by the equation [31]:

$$\log (\theta /1-\theta) = \log K_{ads} + y \log I_{inh} \qquad (8)$$

Where y represents the number of active sites.

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El-Awady isotherm's parameters are shown in Tables (4) & (5). Figure (6) illustrates the linear relationship between log (θ /1- θ) and log (I_{inh}) reveals a linear relationship with a (R^2) values of (0.9448) and (0.9904) for *Berry Mango Leaves Extract* inhibitor and *Mango Leaves Extract* inhibitor respectively. The El-Awady isotherm model is clearly obeyed by the isotherm for the adsorption of *Berry & Mango Leaves Extract* inhibitors on the surface of copper particularly for *Mango Leaves Extract* inhibitor since it's (R^2) value closer to unity than *Berry Leaves Extract* inhibitor.

4.7. Flory-Huggins Adsorption Isotherm

This model describes the degree of feasibility and spontaneity of the adsorption process and assumes the extent of adsorbate coverage on the adsorbent. It featured a parameter written as that represented the extent of the

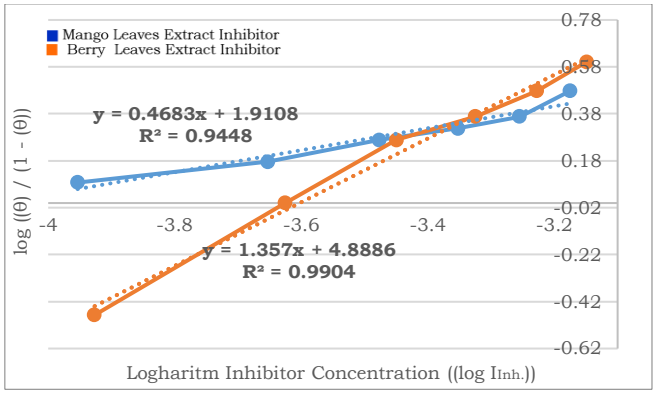

Figure (6) El-Awady Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

adsorbent's surface covering. The general form is provided by Equation [32]:

$$\frac{\theta}{I_{inh}} = K_{ads}\,(1-\theta)^{n} \qquad (9)$$

The linear form of it is expressed:

$$\log \frac{\theta}{I_{inh}} = n + K_{ads} \qquad (10)$$

Where K_{ads} is the Flory-Huggins equilibrium constant (L. mg^{-1}), n is the model exponent, and (θ) is the coverage parameter of the adsorbent surface. Plotting (log (θ/I_{inh})) vs. (log (1 − θ)) is necessary to determine the isotherm parameters, with the slope and intercept standing in for n_{ads} and K_{ads} , respectively. Table (7) showing the parameters of Flory-Huggins isotherm models.

Table (6) The Parameters of Flory-Huggins Isotherm Model for Adsorption of *Berry & Mango Leaves* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

S. No.	*Berry Leaves Extract*				*Mango Leaves Extract*			
	$\frac{\theta}{I_{inh}}$	1 − θ	$\log \frac{\theta}{I_{inh}}$	log 1-θ	$\frac{\theta}{I_{inh}}$	1 − θ	$\log \frac{\theta}{I_{inh}}$	Log 1-θ
1	-	-	-	-	-	-	-	-
2	4942	0.450	3.694	- 0.347	2111	0.750	3.325	- 0.125
3	2695	0.400	3.431	- 0.398	2111	0.500	3.325	- 0.301
4	1947	0.350	3.289	- 0.456	1830	0.350	3.262	- 0.456
5	1519	0.325	3.181	- 0.488	1478	0.300	3.170	- 0.523
6	1258	0.300	3.100	- 0.523	1267	0.250	3.103	- 0.602
7	1123	0.250	3.050	- 0.602	1126	0.200	3.052	- 0.700

Figure (7) depicts the linear relationship between (log (1 − θ)) and (log (θ/I_{inh})). Tables (6) display the characteristics of the Flory-Huggins isotherm for the inhibitors of *Berry* and *Mango Leaves Extract* inhibitors. The obtained (R^2) values were (0.9044) for the *Berry Leaves Extract* inhibitor and (0.8678) for the *Mango leaves Extract* inhibitor, respectively. These values indicates that the *Berry* and *Mango leaves Extract* inhibitors have insufficient adhesion to the copper surface because the (R^2) values are not close to unity.

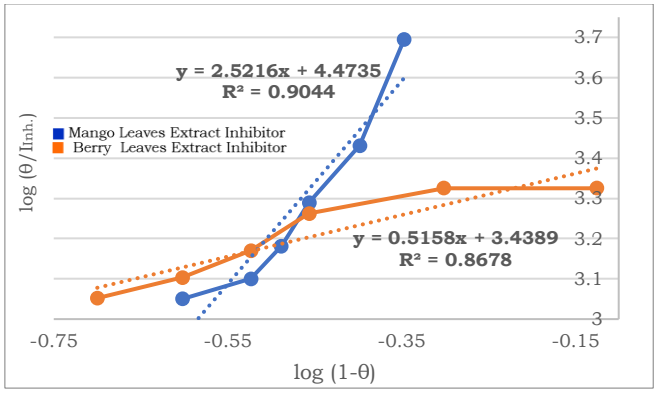

Figure (7) Florry-Huggins Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

4.8. Fowler-Guggenheim Adsorption Isotherm

One of the most straightforward equations that accounts for the lateral interaction of adsorbate molecules is this one. The general form is as follows:

$$(K_{ads})(I_{inh}) = \frac{\theta}{1-\theta}\exp\left(\frac{2\theta W}{RT}\right) \qquad (11)$$

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The linear form of it is expressed:

$$\ln\left(\frac{I_{inh}\,(1-\theta)}{\theta}\right) = \frac{2W}{RT}\,\theta - \ln K_{ads} \qquad (12)$$

Where W is the energy of intermolecular interaction between the molecules of the adsorbate (KJ. mol $^{-1}$) and K_{ads} is the Fowler-Guggenheim equilibrium constant (L. mg $^{-1}$) [33, 34]. The equation's parameters are determined by plotting ln [I_{inh} (1 − θ)/ θ] vs. (θ), as shown in Figure (8). The slope and intercept of this straight line correspond to K_{ads} and W, respectively. Adsorption heat and charge fluctuate linearly. When the values of W are greater than zero, it means that the adsorbate molecules are interacting attractively; however, if the values of W are negative, the adsorbate molecules are interacting repulsionally; and if W = 0, there is no interaction [34]. The Fowler-Guggenheim isotherm parameters for the Berry and Mango Leaves Extract inhibitors are shown in Tables (7).

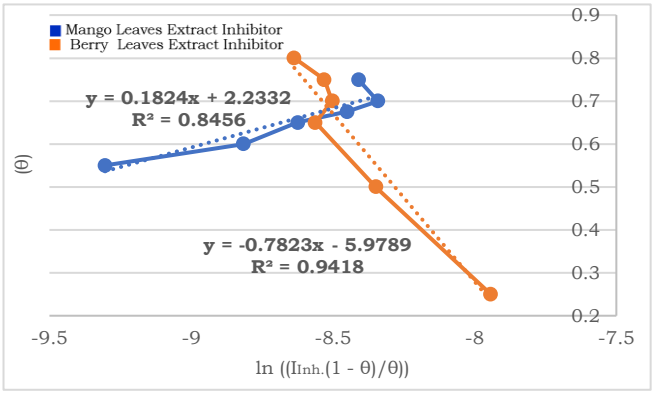

Figure (8) Fowler-Guggenheim Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

Table (8) Fowler-Guggenheim Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

S. No.	$\frac{1}{\theta}$	(1-θ)	I_{inh} x (1 − θ) x10 $^{-5}$	1 / (I_{inh}(1 − θ))	$\frac{1}{\theta}$	(1-θ)	I_{inh} x (1 − θ) x10 $^{-5}$	1 / (I_{inh}(1 − θ))
1	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	1.538	0.650	11.686	8556.882	1.538	0.35	12.432	8043.758
5	1.481	0.675	14.462	6914.434	1.428	0.30	14.208	7038.288
6	1.428	0.700	16.695	5989.817	1.333	0.25	14.800	6756.757
7	1.333	0.750	16.697	5988.920	1.250	0.20	14.206	7039.279

For the *Berry* and *Mango Leaves Extract* inhibitors, the obtained (R^2) values were (0.8456) and (0.9418) respectively. The (R^2) value of the *Berry Leaves Extract* Inhibitor shows that there is no good adsorption on the surface of copper material, whereas the *Mango Leaves Extract* Inhibitor's adsorption on the copper surface material was much better because it is more closely related to unity and is more obeying to the Fowler-Guggenheim adsorption isotherm model. Tables (1) & (7) showing the parameters for Fowler-Guggenheim adsorption isotherm.

4.9. Kiselev Adsorption Isotherm

This model is known as the model of the localized monomolecular layer and is only when θ ≥ 0.68. Its linear expression is [35]:

$$\frac{1}{(I_{inh})(1-\theta)} = Ki\frac{1}{\theta} + Ki\,Kn \qquad (13)$$

where *Ki* is Kiselev's constant (L. mg^{-1}), and *Kn* is the equilibrium constant of complex formation between the molecules of the adsorbate. Constants are calculated by plotting 1/[I_{inh} (1-θ)] vs. 1/θ as shown in Figure (9), where the slope and the intercept represent *Ki* and *Kn*, respectively [35].

In case of Kiselev adsorption isotherm, the chosen data were those which of θ ≥ 0.68. Table (8) showing the parameters for Kiselev adsorption isotherm.

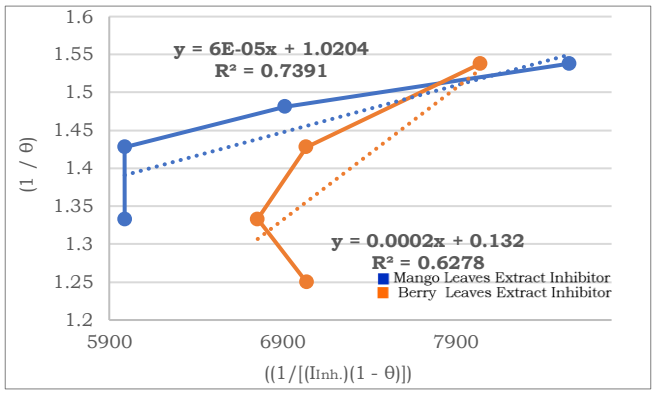

Figure (9) Kiselev Isotherm for Adsorption of *Berry & Mango Leaves Extract* Inhibitors on the Copper Surface in (1 M HNO_3) Solution.

The obtained (R^2) values for the *Berry and Mango Leaves Extract* inhibitors were (0.7391) and (0.6278), respectively. The (R^2) values of the two inhibitors show that there is no

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good adsorption on the surface of copper material since they are far from the unity, and as a result, the *Berry and Mango Leaves Extract* inhibitors are not obeying to the Kiselev adsorption isotherm model.

Generally, according to the values of correlation coefficient (R^2) of the applied isotherm models, the isotherm models are found to be obeying to *Berry & Mango Leaves Extract* Inhibitors. Figure (10) showing a comparison between the correlation coefficient values of whole applied isotherm models.

According to the Figure (10), the maximum value of correlation coefficient (R^2) was (0.9981) which obtained with Lungmir isotherm model for *Mango Leaves Extract* inhibitor was used, while the minimum one was (0.6278) which obtained with Kiselev isotherm model for *Mango Leaves Extract* inhibitor was used. Based on (R^2) values, when comparing the adsorption of the two applied types of inhibitors (*Berry* & *Mango Leaves Extracts*), the adsorption of *Mango Leaves Extract* inhibitor has slightly more adsorption on the copper surface than the *Berry Leaves Extract* inhibitor.

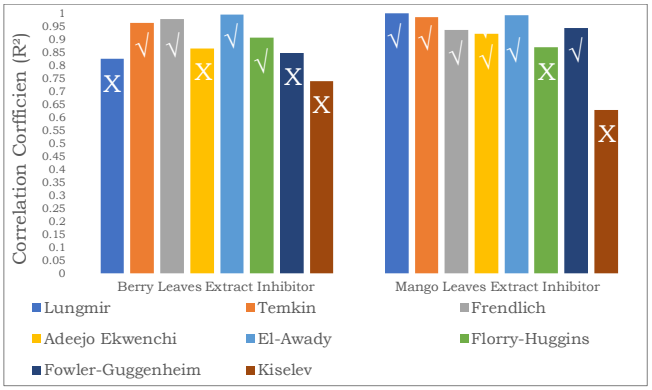

Figure (10) Comparison between the Correlation Coefficient Values of *Berry* & *Mango Leaves Extract* Inhibitors Adsorption Isotherms on the Copper Surface in (1 M HNO_3) Solution.

5. Conclusions

Eight adsorption isotherm models were used to investigate the adsorption behaviour of *Berry & Mango Leaves Extract* inhibitors on the surface of copper material. Based on the obtained correlation coefficient results of the adsorption isotherm plots, the adsorption of *Berry* & *Mango Leaves Extract* Inhibitors on copper surface in (1 M HNO_3) aqueous solution obey to most of the used isotherm models including Lungmuir, Temkin, Frendlich, Adejo Ekwenchi, and El-Awady, Florry-Huggins, Fowler-Guggenheim and finally the Kiselev, the obtained correlation coefficients (R^2) for these models were ranged from (0.7391) to (0.9850) for *Berry Leaves Extract* inhibitor, and (0.6278) to (0.9981) for *Berry Leaves Extract* inhibitor, 0.9759 and 0.9659 respectively. The Temkin isotherm model amongst the others gave the best fit for both inhibitor types since having the highest regression (R^2) value. *Berry* & *Mango Leaves Extract* inhibitors have been identified as they have a very excellent adsorption on the surface of copper. According to the results of adsorption free energy (ΔG°_{ads}) The mechanism of adsorption proposed for the current research used inhibitor was physisorption since the values of (ΔG°_{ads}) are ranged in between (-33.02 to-30.63 kJ. mol^{-1}) and the negative and high values of (ΔG°_{ads}) indicated that there is a strong and spontaneous adsorption of inhibitor on the copper metal surface. Thus, it can be concluded that *Berry* & *Mango Leaves Extract* corrosion inhibition systems were found to be in good agreement with the experimental results as a corrosion inhibitor to protect a surface of copper which has been approved by (*Hamdy Matter*, 2022), and as they have a very excellent adsorption on the surface of copper metal as approved in the present paper research. The present research, approved that the *Mango Leaves Extract* inhibitor has better adsorption on the copper surface comparing to the *Berry Leaves Extract* inhibitor.

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